



Role of oxygen vacancy on the electrical properties of SnO₂-Zn₂SnO₄ ceramic composites with the introduction of Nb₂O₅ oxide



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ABSTRACT

In this work, the role of oxygen vacancy on the electrical properties of traditionally prepared SnO₂-Zn₂SnO₄ ceramic composites was evaluated by introducing Nb₂O₅ oxide. With increasing Nb₂O₅ content, the breakdown electric field $E_{1,0}$ and the relative permittivity ϵ_r measured at low frequencies increased and declined, respectively. In the microstructure photos, the grain size decreased before reaching a saturation point. In addition, Nb was randomly distributed in the grains and along grain boundaries. By doping Nb₂O₅, the color of the sintered samples darkened, and F-type color centers were generated. In the complex electric modulus spectra, the peak of the imaginary part M'' shifted toward a lower frequency; whereas, the activation energy E_a changed slightly with increasing Nb₂O₅ content. The results suggest that oxygen vacancy is the origin of the varistor and high permittivity properties of SnO₂-Zn₂SnO₄ ceramic composites. Furthermore, the varistor and dielectric properties can be modulated by changes in the microstructure.

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1. Introduction

Varistors are important electroceramic materials widely applied in electronic and electrical systems [1]. One kind of varistor, with low breakdown electric field (switch field, $E_{1,0}$, electric field at a current density of 1.0 mA/cm²) and high permittivity, can be used to absorb sparks in electrical micro-machines. In 2005, we found that SnO₂-Zn₂SnO₄ ceramic composites have nonlinear current-voltage properties, characterized by low breakdown voltage and high permittivity [2]. Compared with widely studied SrTiO₃ [3], SnO₂-Zn₂SnO₄ ceramic composites have a much simpler preparation process. The following research revealed that the large amounts of weakly-trapped and electrically diffusible charges that exist in the bulk ceramic are important to the origin of the varistor and high permittivity [4]. Further studies, through heat-treating the samples in vacuum and at atmosphere, indicated that the charges could be oxygen vacancy-related [5]. In ZnO, TiO₂, and SnO₂ varistor systems, Nb₂O₅ has been adopted as a donor doping species, and it can effectively improve the dielectric permittivity and reduce the breakdown electric fields [6–8]. Recently, the parameters of the varistor as well as the high permittivity properties of SnO₂-Zn₂SnO₄ ceramic composites have been greatly improved by doping an optimal amount of SiO₂ [9]. In order to

evaluate the role of oxygen vacancy in SnO₂-Zn₂SnO₄ ceramic composites, the microstructure and electrical properties were studied in this work by introducing Nb₂O₅ to a 0.8 mol SnO₂ + 0.2 mol Zn₂SnO₄ + 0.2 mol SiO₂ composite.

2. Experimental procedures

Ceramic samples with the following compositions: 0.8 mol SnO₂ + 0.2 mol Zn₂SnO₄ + 0.2 mol SiO₂ + x mol Nb₂O₅ ($x = 0.05, 0.10, 0.15$ and 0.20) were prepared using analytical grade SnO₂, ZnO, SiO₂ and Nb₂O₅. The ceramic preparation process and the electrode fabrication method are similar to that used in our previous study [9]. The relationship between current density J and applied electric field E was measured using a Keithley 2410 source meter. The relative permittivity spectra (ϵ_r - f) were measured by Agilent 4294A impedance analyzer in the temperature range of 40–200 °C. The microstructure and distribution of elements were analyzed using a scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS), respectively (Zeiss, Merlin Compact).

3. Results and discussion

Fig. 1 shows the relative permittivity spectra and breakdown electric field for each composition. Because of the DC conductance loss [10,11], ϵ_r decreased sharply when the frequency was lower

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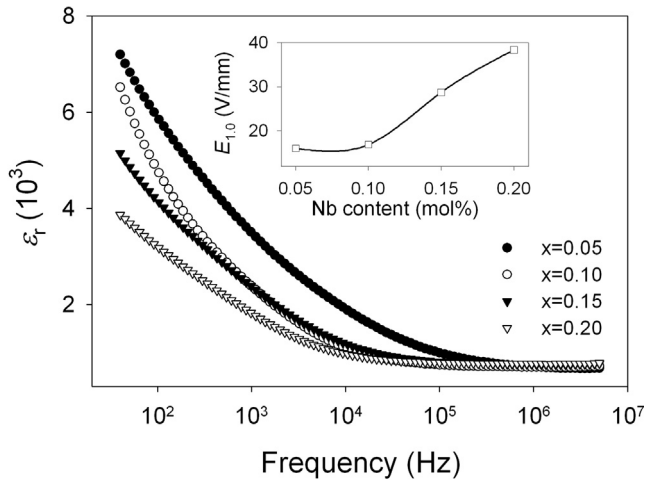
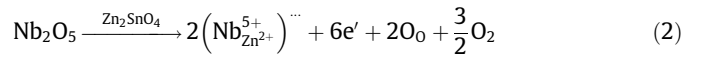
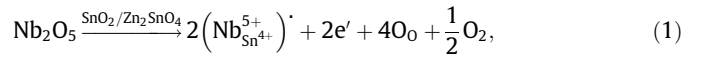


Fig. 1. Spectra of the relative permittivity ϵ_r for each sample. The inset shows the variation of the breakdown electric field $E_{1,0}$ with increasing Nb₂O₅ content.

than 10^5 Hz, whereas it was saturated at high frequencies. With increasing Nb₂O₅ content, ϵ_r decreased at low frequencies, while the saturated ϵ_r at high frequencies changed slightly. As depicted in the inset of Fig. 1, the breakdown electric field $E_{1,0}$ increased gradually with increasing Nb₂O₅ content. Our previous study revealed that ϵ_r is directly and $E_{1,0}$ is inversely proportional to grain size in SnO₂-Zn₂SnO₄ ceramic composites [12]. Thus, the inverse variations of relative permittivity and breakdown electric field,

with increasing Nb₂O₅ content, suggested that doping Nb₂O₅ would inhibit the grain growth.

Fig. 2 shows the SEM images and distributions of Sn, Zn and Nb elements on the sample surface. As expected, the grain size decreased dramatically with increasing Nb₂O₅ content from 0.05 to 0.10 mol%; whereas, no significant decrease was observed by further doping (x = 0.15, 0.20). That is, the grain size did not decrease continuously with increasing Nb₂O₅ content. The results are inconsistent with that discussed in Fig. 1 and indicate that the electrical properties may also be affected by other mechanisms besides grain size. From Fig. 2, it was found that the Nb element distributed randomly in the grains and along grain boundaries. That is, Nb had integrated into the SnO₂ and Zn₂SnO₄ lattices, as described by the following equations:



In SnO₂ varistors, Nb₂O₅ or Ta₂O₅ is a necessary donor dopant to improve the conductivity of SnO₂ grains, as expressed by Eq. (1) [8]. As a result, the breakdown electric field would decline and these donors would improve the relative permittivity [13,14]. Although Nb₂O₅ also acts as donor in SnO₂-Zn₂SnO₄ ceramic composites, the variations of ϵ_r and $E_{1,0}$ are in contrast with the results in SnO₂ varistors. Thus, it is reasonable to assume that the electrons generated in Eq. (1) or (2) have been captured by some defects. As seen in the bottom right of Fig. 2, the color of the sample without Nb₂O₅ doping was ivory white. Conversely the Nb₂O₅

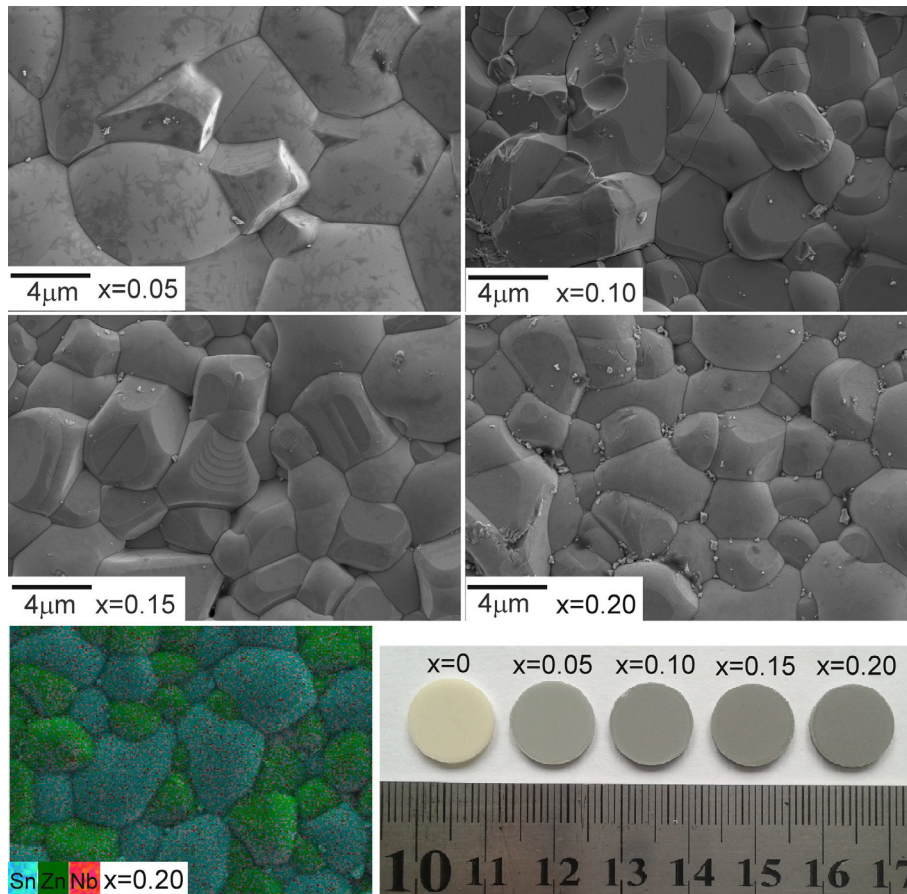


Fig. 2. SEM images, distributions of the elements of Sn, Zn, Nb on the sample surface, and an image of as-sintered samples.

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